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Diffusion of Fluids in Mesoporous Host Materials

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1. Introduction

Since the first report on the synthesis of ordered mesoporous MCM-41 in 1992 [1], the interest to these materials having pore sizes in the range from 2 to 50 nm has continuously been growing. Due to a fascinating match of their structural properties and the adjustability of the surface chemistry, mesoporous materials provide very flexible options for their use in diverse applications in medicine [2], chemistry [3], optics [4], etc. On the other hand, the availability of mesoscopic voids with well-defined geometries and boundary conditions, where tiny molecular or atomic ensembles can be contained, has enabled studying various fundamental processes occurring on the mesoscale. These properties are often found to differ appreciably or even to be absent in the macroscopic systems [5]. Concerning both applications and fundamental studies, dynamics of confined ensembles and molecular diffusion, in particular, may play a decisive role in determining their properties. Therefore, better understanding of the diffusive dynamics of confined fluids is of crucial importance.

Among a variety of techniques adopted to probe translational dynamics in pore spaces, pulsed field gradient nuclear magnetic resonance (PFG NMR) is proven to be especially suitable [6]. In particular, it has recently been demonstrated that by accessing simultaneously both microscopic dynamics, namely the molecular diffusivities, and phase equilibrium, namely the phase composition, the fluid behaviour in porous materials can be addressed in most informative way [7-9].

2. Transport modes of confined fluids

One of the distinct properties of molecular ensembles confined to mesoporous solids is their reach phase behaviour [5]. Thus, different phases may coexist over a wide range of the external conditions. As a consequence of the fact that the diffusivities in solid, liquid and gaseous phases differ notably, complex phase behaviour may, in turn, give rise to complex patterns in the diffusive dynamics. Considering, for example, liquid-gas coexistence in mesoporous solids at low external gas pressures, one may identify two transport modes contributing to the overall mass transfer, namely surface diffusion of the molecules adsorbed on the pore walls [10] and Knudsen diffusion in the gaseous phase. Notably, these two modes are mixed up in a complex way by the molecular exchange process between the two phases. The details of this exchange process are determined by the intermolecular interactions and the geometries of the phases [9,11]. With increasing the gas pressure, the formation of the capillary-condensed domains may substantially complicate the overall dynamics by introducing one more diffusion mode. Thus, the cumulative effect of the variation of the external parameters such as pressure or temperature on the diffusion behaviour results from: (i) changes of the local diffusivities

in the different phases (e.g., due to stretching of the capillary-condensed liquid); (ii) changes of the relative phase composition, (iii) changes of the geometries of the co-existing phases (as indicated by, e.g., the occurrence of the adsorption hysteresis). Albeit such a complexity, a quantitative analysis of the long-time translational dynamics on the length-scales much exceeding a typical pore size is still possible [7,9] and the thus obtained results do reasonably agree with the data of PFG NMR.

3. Microscopic dynamics vs. macroscopic dynamics

One of the widely used approaches to access the diffusivities in porous solids is based on the analysis of macroscopic uptake or release kinetics. The data obtained in this way in microporous materials (zeolites) have often been reported to differ appreciably from the data of direct measurements of the diffusivities using PFG NMR. The discrepancies have been attributed to the existence of additional transport resistances, e.g. surface barriers [12]. Interestingly, in disordered mesoporous materials a similar discrepancy can be observed [8]. However, in this case it originates from a totally different phenomenon, namely strong metastabilities of the phase separation processes under mesoscalic confinements. Joint analysis of the dynamic data of macroscopic and microscopic measurements provides in this systems deeper insight into out-of-equilibrium dynamics and thermodynamics of fluids in disordered mesopores.

4. Conclusion

Although some general tendencies in dynamics of molecular ensembles confined to mesoporous solids and their correlations with the phase state are already established, in particular with the help of nuclear magnetic resonance, many phenomena still remain poorly understood. Their better understanding requires a synergetic exploration of their both dynamic and thermodynamic properties.

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